

Use of Refractory Nanoparticles as a Component of Welding Materials in Welding and Surfacing With Coated Electrodes and Flux Cored Wires

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Abstract. The authors address to the issue of mainstream directions and application fields of nanostructured coated electrodes and flux cored wires, their distinctive advantages and shortcomings. Some consideration is given to use of refractory nanoparticles and their influence on the structure and properties of metal when welding and surfacing with flux cored wires and coated electrodes. The results of research carried out in this sphere are analyzed.

1. Introduction

The beginning of the 21st century is distinguished by the rapid development of nanotechnologies and nano-materials, which are used in the most important fields of human activity and in all advanced economies of the world. The importance of nanotechnologies and nano-materials is highlighted by such contributions to this field as a great number of scientific papers, whose authors deal with the specifics of nano-materials, the intensity of adopting fundamental and applied engineering products, and the growing amount of investments. These activities will be amongst the basic factors of defense, scientific and economic development of the countries in the next decades [1].

The number of scientific papers focused on nano-materials and nano-technologies is quite impressive, since approximately 15-25.000 articles, whose authors address to this range of problems, have been published over the last few years; it is definitely a very significant factor [1].

Mechanical engineering is one of the main industries applying nano-materials. The technologies of synthesizing wear resistant coatings are adopted in this industry; a lot of attention is paid to nanostructured products and equipment for processing workpieces with nanometer accuracy. What is more important, the quality can be improved via applying nano-additives to the certain technological procedures or appropriate welding regimes [2].

At present the technologies of manual and mechanized arc welding are widely used in construction and mechanical engineering. Manual arc welding is the most accepted welding technique, which is always in demand. This welding process meets principal technological criteria and requirements, for instance: exact high quality weld joints with high parameters of strength and functionality are produced on the base of this process. Flux cored wires are becoming widely applied these days for mechanized welding and surfacing. Use of flux cored wires made it possible to eliminate difficulties of welding and surfacing operations when mounting in open workshops and in field conditions, the processes have become twice to five times more efficient, providing high quality weld joints, as



against welding with the solid wire. The number of labor-intensive manual operations to remove metal splatter from structures has been reduced as well [3].

Welding on the base of flux cored wires is currently a promising procedure of mechanized welding capable to improve labor efficiency significantly in comparison with manual arc welding and mechanized welding in shielding gases [2].

It differs from other types of mechanized welding because it combines advantages of both manual arc welding – simplicity, mobility – and those of mechanized welding in shielding gases – high efficiency and quality of produced weld joints [1, 2].

It is interesting to study possibilities of using nano-materials for welding and surfacing with flux cored wires and with coated electrodes simultaneously, since physical characteristics of these processes are similar.

2. Research overview

A flux cored wire is a highly efficient welding material. The advantage of the flux cored wire over the solid wire is its feed rate: the flux cored wire is supplied approximately 20-40% faster as against the solid wire at equal welding currents. Flux cored wires are divided into milled and seamless ones according to their structure [3].

The advantages provided by flux cored wires are highlighted [3]:

- appropriate formation of a weld joint (some grades support backhand welding);
- minimal spattering in proper welding conditions;
- micro-alloying components, ensuring special properties of weld metal, are used in a filler;
- efficiency of welding is at least 1.2 times higher in the flat position and at least 3 times better in vertical and in overhead positions in comparison with the solid wire [4].

In view of weldpool protection from exposure to the atmosphere there are two types of flux cored wires – gas-shielded flux cored wires and self shielded flux cored wires [4].

Flux cored wires are in great demand on the market of welding materials despite their relatively high cost. Since welding and surfacing technologies based on application of flux cored wires are widely accepted in industrial countries, their use in production and building is constantly growing, although short-termed declines are also possible in world economic crises [4].

Special characteristics listed below cause increasing demand for flux cored wires:

1. High efficiency:
 - faster speeds of welding and surfacing;
2. Convenience of application:
 - broad tolerance limits of welding conditions;
 - possibility of fine electrode metal transfer;
3. Low risk of failures when welding:
 - slag and shielding gas provide double protection of a weldpool;
 - minimal risk of weld porosity, even when site welding;
 - low risk of insufficient penetration depth;
4. Reducing total production costs:
 - welding and idle times are shortened;
5. Field of application:
 - possible to use when underwater welding [5].

The configurations of weld penetration are different when using flux cored and solid wires for consumable electrode welding in shielding gases.

Flux cored wires support more gradient junction of weld beds when multilayer welding or surfacing. Provided that welding technology is used in a proper way one can avoid such defects as overlapping gaps between weld beds, pores or slag impurities [4].

Rutile flux cored wires are used in various branches of industry because of their properties, the main of which is high processability [5]:

- welding can be carried out in difficult conditions and requires no special skills of a welder;

- a high quality weld joint is produced in all spatial positions due to quickly hardening rutile slag;
- high surfacing factor is ensured in all spatial positions, especially in a vertical one when bottom-to-top welding (arc current up to 280 A);
- appropriate micro-alloying is possible, which improves viscosity and mechanical properties of a weld joint provided that concentration of alloying elements is minimal;
- welding in CO₂ with little splashing is possible;
- when welding in a gas mixture (82%Ar+18%CO₂) splashing is almost avoided;
- a root weld can be made on a ceramic substrate;
- automatic orbit welding in all spatial position is possible;
- slag coverage is easy removable [4].

New rutile flux cored wires for welding various inter alia thick-walled constructions are developed due to the high factor of surfacing performed in a vertical position from the bottom to the top [4].

Using a flux cored wire with the charge mixture, containing certain materials, provides modification of a surfaced metal with the components of the charge mixture, so its structure is a fine grained one, and excess phases are distributed uniformly, making the surfaced metal wear resistant. Alloying of the surfaced metal by the components of the flux cored wire results in formation of an oversaturated aluminum solid solution, as the consequence, the properties of the surfaced layer are better than those of the substrate [15].

The effect of refractory materials on mechanical properties of the surfaced metal is an urgent issue requiring deeper investigation in the present day mechanical engineering. It is proposed to add nano-disperse refractory compounds to the filler of a flux cored wire used for surfacing components subject to the abrasive wear, for welding and surfacing thermally stable alloys. These compounds can provide synthesizing the surfaced metals with certain properties. Heat stability tests of the surfaced metal show that nano-disperse refractory compounds used in flux cored wire fillers improve thermal stability of the surfaced metal – the number of cycles “heating - cooling” is increased till a crack network appears and propagates [10, 11]. Abrasive wear resistance tests have revealed that samples produced using the flux cored wire with a definite charge composition are more wear-resistant as against the samples made of the standard flux cored wires [11].

The development of new welding materials with a high-resistant structure, supporting their utilization in aggressive conditions with thermal and force impact, is a burning issue of the present day mechanical engineering. It is a well-known fact that surfaced metals and cast alloys modified by nano-particles of refractory chemical compounds have improved service and process characteristics. Therefore, welding and surfacing technologies based on adding nano-particles of refractory compounds to the weldpool are in a progress [7].

The authors [6] have emphasized that the fine-grain structure of a weld or the surfaced layer is formed due to adding the certain quantity of nano-particles of refractory compounds, so such properties as hardness and wear resistance are improved this way.

Nano-particles can be added in different ways when mechanized or automatic welding or surfacing:

- nano-particles are injected into a shielding gas;
- nano-particles are a component of a flux cored wire;
- a wire can be coated with nano-particles.

As manual arc welding is the most common welding procedure, the study is to be focused on welding and surfacing by coated electrodes containing nano-materials.

The powders with ultradisperse particles can be added to the coated electrodes in the following ways:

- powders are added to the mixed envelope before coating the rod;
- modifying powders are added to the liquid glass [7].

There are certain results available in research into the effect of nano-particles of refractory compounds on the structure and properties of metal.

For instance, in the work by G.N. Sokolov titanium carbonitride powders TiCN with particles 80 to 500 nm are used as nano-components added to fillers of flux cored and compounded wires when

surfacing. Microparticles (60 μm) of nickel powder (99.9%) being the component of the wire mixture are used to transport nano-particles into the weldpool. Nano-particles TiCN are added to Ni particles when their co-processing in a planetary-type mill, resulting in obtaining composite nickel granules. The share of nano-particles in composite nickel granules is 30 wt. % for TiCN. These powders are used to produce flux cored and compounded wires with diameter 3 mm and steel 08 KP envelope, which contain 0.1 – 0.6 wt. % refractory nano-particles. A layer of the surfaced metal on the base of iron: heat-resistant nitrogen-containing alloy 15Cr15Ni4AlMn3 is made with these wires when electroslag hard-facing with the fluoride flux ANF-6 and argon-arc surfacing [7].

The study based on the electron microscopy has revealed that the number of spherical intermetallic particles 0.5 to 1.5 μm grows, as well as their distribution is more homogenous in the austenite-martensite structure of the alloy 15Cr15Ni4AlMn3 produced when argon-arc surfacing by the flux cored wire with refractory nano-particles TiCN. Here, the average grain in the metal is 2.5 times smaller as against that of the initial structure, and its strain and cracking resistance gets better when thermal fatigue testing. [7].

The improved mechanical properties of alloys surfaced by refractory nano-particles are possible due to the forming composite structure with spherical intermetallic particles as its basic elements. Electron microscopy analysis of the sections of these intermetallic particles, prepared via ion etching has shown a lot of aggregates of 5 to 50 nm nano-particles. The space between them is 20 to 150 nm. Taking into consideration the dimensions of intermetallic particles we can assume that the number of nano-particles can vary from some hundreds to thousands [7].

The purpose of the work [8] by A.A. Artemyev and G.N. Sokolov is to study the importance of nano-particles TiCN, added to the flux cored wire for formation of the man-made composite structure and properties of the wear resistant layer of the electroslag surfaced metal. The flux cored wire is added to the slag ANF-6 through a hollow electrode. Modifying the surfaced metal requires adding up to 2 wt. % composite powder to the mixture of experimental flux cored wires. The powder contains 70 wt. % nickel micro-powder with grains less 60 μm . The particles of nickel contain 30 wt. % implanted ultradisperse refractory particles TiCN with grains less 80 nm [8].

The metallographic study has identified that structure and phase composition of the added metal based on matrix 20Cr7Mn12Ni2 is different for various concentration of the boride added to the flux cored wire. 28 wt. % concentration of TiB₂ is the cause of a hypoeutectic structure. Boride eutectic based on α -Fe and residual austenite has the microhardness ranging from 12 to 15.5 GPa [8].

Reduced mass share of powder TiB₂ in the wire filler to 18 wt. % is the cause of the eutectic structure with low microhardness (6.7 – 7.5 GPa) and a considerable dispersion. Hardness of the surfaced metal is also decreased and approximates to 45 – 48 HRC [8].

Decreasing the concentration of TiB₂ to 8 wt. % influences on the structure of the surfaced metal, so it consists of alloyed austenite grains with microhardness of 4 – 5 GPa surrounded by separated boride eutectic. Its hardness is low 17 – 20 HRC because of the little eutectic in soft and lamellar austenite matrix [8].

Abrasive wear resistance tests have identified that the 3.5 – fold rise of TiB₂ concentration in the mixture of the flux cored wire results in 2.5 – fold increase of wear resistance of the surfaced metal [8].

Artemyev and Sokolov [8] have revealed dissolution and coagulation of some nano-particles TiCN when electroslag surfacing. Then colonies of coarse irregular particles 1-3 μm are formed. Relying on the atomic-force microscopy the authors have detected that there are impurities 15 to 50 nm in the layer of the surfaced metal. Some particles TiCN fail to get dissolved in the melt and are the centers of crystallization for other titanium compounds. The relative wear resistance is improved more than twice as compared with the reference alloy, its value exceeds fivefold the one of the best industrial wear resistant alloys, surfaced with the standard wire PP Np-170M (15Cr15B3T2) [8].

The authors of the paper [9] A.M. Levchenko, S.G. Parshin and I.S. Antipov faced the problem of synthesizing the flux cored wire for mechanized underwater welding of steels. This wire is manufactured via plastic deformation of a band of steel 08kp according to GOST 3560–73, the

mixture is filled, followed by wire removal as soon as the required diameter 1.6 mm is obtained. The mixture consists of ore mineral and chemically pure compounds with a regular granulometric composition, having the coefficient of flux cored wire filling 30 – 35%. Nano-composite material is surfaced electrochemically through colloid sulphate electrolytes, containing nano-disperse particles of halogenide salts and oxides [9].

The authors [9] have pointed at modified structure of the surfaced metal provided that the concentration of TiCN particles in the wire filler exceeds 0.2 wt. % - the grains get smaller 2.0-2.5 times on the average. We can assume that thermodynamically high-stable nano-particles of titanium carbonitride, being slightly dissolved in a metal melt, pass from the mixture of the flux cored wire into the weldpool, and influence the crystallization kinetics of the surfaced metal.

The research into structures has revealed that the increased (more 0.5 wt. %) concentration of the nanostructured powder TiCN in the filler of the flux cored wire is the cause of relatively coarse (up to 2µm) titanium carbonitride impurities, forming in the modified structure of the surfaced metal. These impurities are quite natural and their origination is regarded as melting smaller (less 30 nm) particles of nanostructured powder, their melting temperature can be below 2400 °C. This process occurs at the stage of melting and transfer of electrode metal drops, the temperature of drops is 2500 °C [9].

It is found out in the paper that coarse (more 2 µm) impurities of titanium carbonitride are stress raisers, which deteriorate its fatigue strength considerably. Therefore, the concentration of source nanostructured powder in the mixture of the flux cored wire can not exceed 0.5 w. % [9].

The research into welding and process properties of flux cored wires has revealed that the wire III-ΠC is distinguished by the uniform melting of envelope and rode, atomized transfer of the electrode metal, it provides welds of a good quality when low, horizontal and vertical underwater welding [9].

S.G. Parshin provides the description of applying nano-disperse particles of activating fluxes and nanostructured electrode materials [12 – 14]. These works are focused on the improvement of welding efficiency, characteristics of electrode metal drop transfer and quality of the weld joints of steel. It is found out that nanostructured fluxes make it possible to control the arc energy properties, improve the transfer of electrode metal drops and quality of the weld joints of steel [12, 13]. The use of the developed nanostructured electrode wires coated with the micro-composite mixture containing halogenide particles in the metallic matrix allows of developing the forced MIG technology – welding of steels, distinguished by the improved efficiency of the process up to до 68.5 %. The weld joints made according to this new technology are characterized by stable formation under deep penetration of the plate rolled metal, even in critical and supercritical conditions at high current densities [14, 25].

The paper [16] by V.B. Litvinenko – Arykov et al is concentrated on the influence of titanium carbonitride nano-powder TiCN, put into the mixture of flux cored wires, on the structure of the surfaced metal and its properties. The composition of the metal is similar to that of high strength austenite-martensite alloys on the base of iron. Flux cored wires with the diameter of 2.6 mm are used for surfacing; the coefficient of filling the mixture is 46 - 47 %. The wires are produced on the base of a well-known technology. The powder of nitrated chromium is added to the filler of the flux cored wires to make a layer of the surfaced metal. For the purpose of the research a composite micro-powder, produced in the Institute of Metallurgy and Materials by A.A. Baykov, is used to provide uniform distribution of TiCN nano-particles in the filler of the flux cored wire. The results have demonstrated that 0.2 – 0.5 (wt. %) of TiCN nanostructured powder added to the mixture of the flux cored wires cause 2.0 – 2.5 fold grinding of grains. Nano-dimensional and micro-disperse TiCN particles in the metal, which is subjected to surfacing support the resistance to plastic deformation at rather high temperatures 750 to 950 °C.

The works [17] by G. N. Sokolov and I.V. Lysak et al are focused on modifying the structure of the surfaced metal by the nanostructured tungsten carbides. The material to transport the particles of tungsten carbide is nano-disperse powder of nickel (99.9 % Ni) with particles 50 – 80 µm. As the result nickel granules are synthesized, which contain approximately 30 wt. % nano-carbides. The shielding coating of the electrode is made of the mixture containing these granules and potassium-sodium liquid glass. For the experiment they use electrodes OK 43.32 – rutile electrodes for welding

low carbon steels (ESAB Group Limited) and UTP 67 S – basic electrodes applied for surfacing the wear resistant alloy (UTP Sweissmaterial GmbH). These electrodes provide the following chemical composition of the surfaced metal (wt. %) C – 0.07; Si – 0.4; Mn – 0.5 and C – 0.5; Cr – 9.0; Si – 3.0; Mn – 0.5, respectively, iron is the base with impurities making the rest. The rods with the diameter 2 mm are coated by the mixture containing nickel carbide granules. The rods are made of wire Sv-06X19H9T. In the process of experiments steel 20 plates are surfaced. First, the structure of the layer surfaced by coated electrodes OK 43.32 is a ferritic pearlite mixture. The addition of nickel and tungsten nano-carbides results in the change of metal, which becomes a modified sub-dispersed solid solution on the base of α -Fe and residual austenite on the grain boundaries. The number of non-metallic impurities, distributed unevenly in the metal and having indefinite boundaries is decreased by 15-20 %. The other nonmetallic impurities are distributed more uniformly and have a globular form. This type of metal structure is to further the improvement of its plasticity and reliability at low temperatures and under cyclic loads. In the process of research into the metal structure, surfaced by electrode UTP 67 S with alloying coating no significant changes of its structure and hardness are revealed. This phenomenon can be referred to the specifics of poorly studied and complex processes of carbon diffusion, occurring in the metal with carbide nano-particles. More efficient influence on the structure of the surfaced metal requires the production of electrodes and wires, containing nano-disperse particles of other refractory materials.

Welding with flux-covered wires and manual arc welding with coated electrodes are somehow similar. Both procedures require the use of powdered components. In the flux-covered wire there are shielding components in the metallic envelope, but on the rod as a coating when manual arc welding. Therefore, it is interesting to study the influence of nano-particles when welding and surfacing both by flux cored wires and coated electrodes.

The paper [18] by S.O. Gordin, A.N. Smirnov and V.L. Knyazkov provides the description of adding 2.0% titanium carbonitride powder to the coating of electrodes (T-590), which contains ferrochromium, ferroboron, marble, ferrosilicon, fluor spar, ferromanganese, graphite, and potash, to improve the wear resistance of the surfaced coating, operated in conditions of the abrasive wear. When producing the electrodes for the purpose of experiments the nanostructured powder of titanium carbonitride with particles of 60 to 200 nm is added to the coating. The coating is put on the steel Sv-08A rods with the diameter of 4.0 mm. This chemical composition improves the plasticity of the coating mixture. The hardness of the surfaced alloy is up to 66 HRC, with improved wear resistance coefficient and long service life of the remanufactured products. The particles of titanium carbonitride are a refractory compound ($T_{ml} \sim 3100^{\circ}\text{C}$), they improve the toughness of the liquid weld pool metal, increase the rate of metal crystallization and allow of synthesizing a solid solution with martensite-carbide or dendrite structure, reinforced by hard wear resistant phases.

The wear resistance coefficient of the coating made by electrodes containing the nano-powder of titanium carbonitride in the envelope is higher by 57% than that of the coating made by serial electrodes. To identify the thermal stability of the surfaced layer produced by serial and experimental electrodes, hot samples are cooled in water after making a layer. No cracks and delamination are detected when testing the surfaced layers reinforced by carbonitride [18].

The purpose of the work [19, 20] by G.N. Sokolov, A.A. Troshkov et al is to study the influence of nickel micro-granules with nano-disperse tungsten carbide (WC) particles, added to the coatings of welding electrodes, on the structure, impact strength and hardness of the surfaced layer of low carbon metal. The experimental electrodes are manufactured via adding granules of a composite powder to the base coating of industrial electrodes UONI – 13/45 with the diameter of 3 mm. In the process of metallographic study on the surfaced metal and the solidified slag it is revealed that some composite nickel micro-granules get stuck in the viscous slag when passing through the gas-slag environment of the welding reaction zone, but most of them get into the molten metal and alloys it. Tungsten, nickel and carbon are distributed quite uniformly among components of the surfaced metal structure. Their concentration in the local micro-volumes of the alloy depends on the dimensions of the composite nickel granules, quantity and distribution of WC carbide nano-particles added to them. Therefore,

addition of composite nickel micro-granules containing nano-disperse tungsten carbide to the base coating of the welding electrodes, is an efficient procedure to modify the low carbon surfaced metal. The concentration of micro-granules Ni + WC (approximately 3 wt. %) in electrode coating supports the improved impact strength of the weld metal as against the samples made by standard electrodes UONI – 13/45. [21, 23, 24]

3. Conclusions

Having analyzed the studies above the results of adding nanostructured powders to the weldpool when arc welding are highlighted:

- the surfaced layer of metal gets modified;
- such characteristics as impact strength and hardness of the weld metal are improved;
- grains in the heat impact area get smaller;
- improvement of arc properties;
- improved formation of the weld;
- increased efficiency of welding.

The results of the literature review demonstrate that nanostructured particles of refractory compounds added to the weldpool when welding and surfacing further the formation of fine grain structure of metal due to crystallization centers developed by refractory materials particles.

Refractory particles added when surfacing have a positive effect on the abrasive wear resistance of the surfaced layer.

Flux cored wires and coated electrodes with nano-particles of refractory compounds are distinguished by satisfactory process characteristics.

One of the prospects of welding and surfacing procedures based on nano-materials is the development of new types of composite wires. Newly developed welding materials are to meet both the process requirements and economic reasonability of use in a particular product. The achievement of the purpose requires solution of the following problems: to design a device and manufacturing procedure of a composite flux cored wire with a complex chemical composition; to determine welding and process characteristics of the developed wires; to reveal the character of influence of new welding materials on the structure and properties of the surfaced metal; to estimate the economic efficiency of adoption new flux cored wires in the industry.

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